

What is claimed is:

1. An improved process for preparing a crosslinked article of manufacture comprising the steps

(a) melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier,

at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species;

(b) forming an article of manufacture from the crosslinkable polymeric composition; and

(c) crosslinking the crosslinkable polymeric composition at the nominal crosslinking temperature as a formed article of manufacture.

2. The improved process of Claim 1 wherein the free-radical crosslinkable polymer being hydrocarbon-based.

3. The improved process of Claim 1 wherein the free-radical crosslinkable polymer is selected from the group consisting of ethylene/propylene/diene monomers, ethylene/propylene rubbers, ethylene/alpha-olefin copolymers, ethylene homopolymers, ethylene/unsaturated ester copolymers, ethylene/styrene interpolymers, halogenated polyethylene, propylene copolymers, natural rubber, styrene/butadiene rubber, styrene/butadiene/styrene block copolymers, styrene/ethylene/butadiene/styrene copolymers, polybutadiene rubber, butyl rubber, chloroprene rubber, chlorosulfonated polyethylene rubber, ethylene/diene copolymer, and nitrile rubber, and blends thereof.

4. The improved process of Claim 3 wherein the free-radical crosslinkable polymer being a propylene polymer and the crosslinking temperature profile modifier suppresses chain scission of the propylene polymer.

5. The improved process of Claim 1 wherein the free-radical inducing species being selected from the group consisting of organic peroxides, Azo free radical initiators, bicumene, oxygen, and air.

6. The improved process of Claim 1 wherein the crosslinking temperature profile modifier being a free radical inhibitor.
7. The improved process of Claim 6 wherein the free radical inhibitor being selected from the group consisting of (i) hindered amine-derived stable organic free radicals, (ii) iniferters, (iii) organometallic compounds, (iv) aryl azoxy radical, and (v) nitroso compounds.
8. The improved process of Claim 7 wherein the free radical inhibitor being a hindered amine-derived stable organic free radical selected from the group consisting of 2,2,6,6,-tetramethyl piperidinyl oxy (TEMPO) and derivatives thereof.
9. The improved process of Claim 8 wherein the stable organic free radical being a derivative of 2,2,6,6,-tetramethyl piperidinyl oxy selected from the group consisting of bis-TEMPOs, oxo-TEMPO, 4-hydroxy-TEMPO, esters of 4-hydroxy-TEMPO, polymer-bound TEMPO, PROXYL, DOXYL, di-tertiary butyl N oxyl, dimethyl diphenylpyrrolidine-1-oxyl, 4 phosphonoxy TEMPO, and metal complexes with TEMPO.
10. The improved process of Claim 7 wherein the free radical inhibitor being an iniferter selected from the group consisting of tetraethyl thiuram disulfide, benzyl NN diethyldithiocarbamate, dithiocarbamates, polythiocarbamates, and S benzyl dithiocarbamate.
11. The improved process of Claim 1 wherein the crosslinkable polymeric composition achieves the same degree of cure or a higher degree of cure than the combination would achieve in the absence of the crosslinking-temperature-profile modifier.
12. The improved process of Claim 1 wherein the crosslinkable polymeric composition further comprises a cure booster.
13. The improved process of Claim 1 wherein the free-radical crosslinkable polymeric composition further comprises a catalyst for increasing free-radical formation, selected from the group consisting of tertiary amines, cobalt naphthenate, manganese naphthenate, vanadium pentoxide, and quaternary ammonium salt.

14. An improved process for preparing a crosslinked article of manufacture comprising melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier,

at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species.

15. An improved process for preparing a crosslinked article of manufacture comprising the steps

(a) melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier,

at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species;

(b) forming an article of manufacture from the crosslinkable polymeric composition; and

(c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture at a temperature above the nominal crosslinking temperature of the combination of the free-radical crosslinkable polymer and the free-radical inducing species.

16. An improved process for preparing a crosslinked article of manufacture comprising the steps

(a) melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier,

wherein

- (i) in the absence of the crosslinking-temperature-profile modifier, a combination of the free-radical crosslinkable polymer and the free-radical inducing species has a nominal processing rate and
- (ii) the crosslinking-temperature-profile modifier permits running the process at least about 5 percent faster than the nominal processing rate, and

at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species;

- (b) forming an article of manufacture from the crosslinkable polymeric composition; and
- (c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture.

17. The improved process of Claim 16 wherein the crosslinking step occurs at a temperature greater than the nominal crosslinking temperature.

18. An improved process for preparing a crosslinked article of manufacture comprising melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier,

wherein (i) in the absence of the crosslinking-temperature-profile modifier, a combination of the free-radical crosslinkable polymer and the free-radical inducing species has a nominal processing rate and (ii) the crosslinking-temperature-profile modifier permits running the process at least about 5 percent faster than the nominal processing rate,

at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species.

19. An improved process for preparing a crosslinked article of manufacture comprising the steps

- (a) melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer that forms free radicals when subjected to shear energy, heat, or radiation, and
 - (2) a crosslinking-temperature-profile modifier,
- at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species;
- (b) forming an article of manufacture from the crosslinkable polymeric composition; and
 - (c) crosslinking the crosslinkable polymeric composition at the nominal crosslinking temperature as a formed article of manufacture.

20. An improved process for preparing a crosslinked article of manufacture comprising melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer that forms free radicals when subjected to shear energy, heat, or radiation, and
 - (2) a crosslinking-temperature-profile modifier,
- at a melt processing temperature greater than the nominal melt processing temperature of a combination of the free-radical crosslinkable polymer and the free-radical inducing species.

21. The improved process of any of Claims 19 or 20 wherein the temperature of the melt processing temperature portion being raised by increasing the shear energy.

22. The improved process of any of Claims 1 – 21 wherein, at the melt processing temperature, the induction time being at least equal to the nominal induction time.

23. An improved process for preparing a crosslinked article of manufacture comprising the steps

- (a) melt processing a crosslinkable polymeric composition comprising
 - (1) a free-radical crosslinkable polymer,
 - (2) a free-radical inducing species, and
 - (3) a crosslinking-temperature-profile modifier wherein TS1 being an indication of premature crosslinking of a combination of the free-radical crosslinkable polymer and the free-radical inducing species,

at a melt processing temperature greater than the nominal melt processing temperature while maintaining TS1 at least equal to the TS1 of a combination of the free-radical crosslinkable polymer and the free-radical inducing species at the nominal melt processing temperature

- (b) forming an article of manufacture from the crosslinkable polymeric composition; and
- (c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture.

24. An improved process for preparing a crosslinked article of manufacture comprising melt processing a crosslinkable polymeric composition comprising

- (1) a free-radical crosslinkable polymer,
- (2) a free-radical inducing species, and
- (3) a crosslinking-temperature-profile modifier wherein TS1 being an indication of premature crosslinking of a combination of the free-radical crosslinkable polymer and the free-radical inducing species,

at a melt processing temperature greater than the nominal melt processing temperature while maintaining TS1 at least equal to the TS1 of a combination of the free-radical crosslinkable polymer and the free-radical inducing species at the nominal melt processing temperature.

25. The improved process of any of Claims 23 or 24 wherein TS1 of the combination being at least 20 minutes.

26. The improved process of any of Claims 23 or 24 wherein, at the melt processing temperature, the processing rate being at least about 5 percent faster than the nominal processing rate.

27. An improved process for preparing an expanded, crosslinked article of manufacture comprising the steps of

- (a) injecting at an injection temperature an expandable, free-radical crosslinkable polymeric composition of into a mold at a mold temperature, wherein the expandable, free-radical crosslinkable polymeric composition comprises
 - (A1) a free-radical crosslinkable polymer;
 - (A2) a free-radical inducing species;

- (A3) a crosslinking-temperature-profile modifier; and
- (A4) a blowing agent selected from the group consisting of chemical blowing agents and physical blowing agents;
- (b) heating the expandable, free-radical crosslinkable polymeric composition for a period of time to a crosslinking temperature sufficient to expand and crosslink the expandable, crosslinkable polymeric composition;
- (c) removing the expandable, free-radical crosslinkable polymeric composition from the mold; and
- (d) expanding and crosslinking the expandable, free-radical crosslinkable polymeric composition to an expanded, crosslinked article of manufacture.

28. An improved process for preparing an expanded, crosslinked article of manufacture comprising the steps of

- (a) injecting at an injection temperature an expandable, free-radical crosslinkable polymeric composition into a mold at a mold temperature, wherein the expandable, free-radical crosslinkable polymeric composition comprises
 - (A1) a free-radical crosslinkable polymer;
 - (A2) a free-radical inducing species;
 - (A3) a crosslinking-temperature-profile modifier; and
 - (A4) a chemical blowing agent;
- (b) heating the expandable, free-radical crosslinkable polymeric composition in the mold for a period of time to the activation temperature of the blowing agent;
- (c) expanding the expandable, free-radical crosslinkable polymeric composition to an expanded, free-radical crosslinkable polymeric composition in the mold; and.
- (d) crosslinking the expanded, crosslinkable polymeric composition to an expanded, crosslinked polymeric composition in the mold.

29. An article of manufacture prepared from the improved process of any of Claims 1 - 28.

30. A free-radical crosslinkable polymeric composition comprising:

- (a) a free-radical crosslinkable polymer having a melting point at least greater than 130 degrees Celsius and

- (b) a crosslinking-temperature-profile modifier.
31. A free-radical crosslinkable polymeric composition comprising:
- (a) a free-radical crosslinkable polymer blend being susceptible to premature crosslinking at the blend's nominal melt processing temperature and
 - (b) a crosslinking-temperature-profile modifier.
32. The free-radical crosslinkable polymeric composition of Claim 31 wherein the free-radical crosslinkable polymer blend comprises a linear low density polyethylene and a branched polyethylene.
33. A free-radical crosslinkable polymeric composition comprising:
- (a) a free-radical crosslinkable polymer, and
 - (b) a crosslinking-temperature-profile modifier excluding 2,2,6,6,-tetramethyl piperidinyloxy and derivatives thereof.
34. An expandable, free-radical crosslinkable polymeric composition comprising:
- (a) a free-radical crosslinkable polymer;
 - (b) a free-radical inducing species;
 - (c) a crosslinking-temperature-profile modifier; and
 - (d) a blowing agent selected from the group consisting of chemical blowing agents and physical blowing agents.
35. A power cable accessory comprising a free-radical crosslinked polymer composition prepared from a composition comprising
- (a) a free-radical crosslinkable polymer selected from the group consisting of ethylene/propylene/diene monomers, ethylene/propylene rubbers, and mixtures thereof, in an amount between about 20 weight percent and about 90 weight percent,
 - (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
 - (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
 - (d) inorganic fillers in an amount between about 10 weight percent and about 70 weight percent.
36. A power cable comprising a crosslinked insulation prepared from a free-radical crosslinkable polymer composition comprising

- (a) a free-radical crosslinkable polymer selected from the group consisting of ethylene/propylene/diene monomers, ethylene/propylene rubbers, and mixtures thereof, in an amount between about 20 weight percent and about 90 weight percent,
- (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
- (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
- (d) inorganic fillers in an amount between about 10 weight percent and about 70 weight percent.

37. A power cable comprising a crosslinked, flame retardant insulation prepared from a free-radical crosslinkable polymer composition comprising

- (a) a free-radical crosslinkable polymer selected from the group consisting of ethylene/alpha-olefin copolymers, ethylene/unsaturated ester copolymers, and mixtures thereof, in an amount between about 10 weight percent and about 85 weight percent,
- (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
- (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
- (d) flame retardants in an amount between about 15 weight percent and about 70 weight percent.

38. A power cable comprising a crosslinked, semiconductive insulation shield prepared from a free-radical crosslinkable polymer composition comprising

- (a) a free-radical crosslinkable polymer selected from the group consisting of ethylene/alpha-olefin copolymers, ethylene/unsaturated ester copolymers, and mixtures thereof, in an amount between about 10 weight percent and about 85 weight percent,
- (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
- (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
- (d) a conductive filler in an amount between about 20 weight percent and about 40 weight percent.

39. A power cable comprising a crosslinked insulation prepared from a free-radical crosslinkable polymer composition comprising
- (a) a free-radical crosslinkable polymer blend, comprising a linear low density polyethylene and a branched polyethylene, in an amount between about 20 weight percent and about 90 weight percent,
 - (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
 - (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
 - (d) inorganic fillers in an amount between about 10 weight percent and about 70 weight percent.
40. A power cable comprising a crosslinked jacket prepared from a free-radical crosslinkable polymer composition comprising
- (a) a free-radical crosslinkable polymer being chlorinated polyethylene and present in an amount between about 20 weight percent and about 90 weight percent,
 - (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
 - (c) a crosslinking-temperature profile modifier in an amount between about 0.1 weight percent and about 5 weight percent, and
 - (d) inorganic fillers in an amount between about 10 weight percent and about 65 weight percent.
41. A shoe sole comprising an expanded, free-radical crosslinked polymer composition prepared from a composition comprising
- (a) a free-radical crosslinkable polymer being an ethylene/unsaturated ester copolymer in an amount between about 10 weight percent and about 85 weight percent,
 - (b) a free-radical inducing species in an amount between about 0.5 weight percent and 10 weight percent,
 - (c) a crosslinking-temperature profile modifier in an amount between about 0.01 weight percent and about 5 weight percent, and
 - (d) a blowing agent selected from the group consisting of physical blowing agents and chemical blowing agents.